

Task 3 Technical Report
For
Mercury Removal in a Non-Thermal, Plasma-Based
Multi-Pollutant Control Technology for Utility Boilers

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Abstract

ECO process chemistry is initiated by the oxidation of gaseous pollutants (Hg, NO_x and SO₂) in a dielectric barrier discharge reactor. The goal of Task 3, as described in the Cooperative Agreement *Statement of Work*, was to determine the effect of dielectric barrier discharge operating parameters and inlet Hg concentration on mercury oxidation and removal. Results are presented for the oxidation of elemental mercury at several flue gas flow rates (1500, 2000, and 2500 scfm), reactor energy densities (0, 15, 20, and 25 watts/scfm), and a range of inlet elemental mercury levels (0 – 8 ug/Nm³). The testing shows that the DBD reactor can oxidize up to 75% of the elemental Hg under the conditions tested. The testing also shows that mercury speciation in the duct and in the PS Analytical Hg CEMs equipment is altered by reactive ash when high ash loading conditions are present. Results for speciation measurements under high (slip stream prior to ESP with minimal treatment) and normal ash loading (slip stream taken after ESP) are also reported.

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1.0 Introduction

The goal of Task 3 was to investigate the effect of the dielectric barrier discharge reactor operating parameters and inlet mercury concentrations on mercury removal by the ECO[®] process. Parametric testing looked at the effects of energy density requirements, inlet mercury concentration, and velocity through the system on the ability of the dielectric barrier discharge reactor to oxidize elemental mercury in a flue gas stream.

Executive Summary

Oxidation of elemental mercury using the ECO barrier discharge reactor was investigated as part of the cooperative agreement for Mercury Removal in a Non-Thermal, Plasma Based Multi-Pollutant Control Technology for Utility Boilers conducted at the ECO pilot installed at FirstEnergy's Burger Power Plant. The investigation required addition of elemental mercury to the flue gas stream as a result of the low elemental mercury fraction ($< 1 \mu\text{g}/\text{Nm}^3$) of the total mercury content in the Burger power plant flue gas. In addition, the investigation was hampered by the inability to consistently and reliably measure the elemental mercury concentration in the inlet flue gas. This was due to the reactive nature of the ash in the power plant flue gas, causing oxidation of elemental mercury in the ductwork and in the ash removal portion of the mercury sampling train.

The testing showed up to 75% oxidation of elemental mercury by the barrier discharge reactor at an inlet elemental mercury concentration of $8 \mu\text{g}/\text{Nm}^3$ and a barrier discharge reactor energy density of 25 w/scfm. Tests were conducted over a range of flue gas flowrates and dielectric barrier discharge reactor power levels.

1.1 Motivation

According to EPA's 1999 National Emissions Inventory, coal-fired electric power plants are the largest source of anthropogenic mercury air emissions in the United States. These power plants account for approximately 40% of total U.S. manmade mercury emissions. On December 15, 2003, the Environmental Protection Agency (EPA) proposed a rule to permanently cap and reduce mercury emissions from power plants. The EPA is proposing two alternatives for controlling emissions of mercury from utilities. The first proposed rule requires utilities to install controls known as “maximum achievable control technologies” (MACT) under section 112 of the Clean Air Act. If implemented, this proposal would reduce mercury emissions from U.S. coal-burning power plants nationwide by 14 tons (29 percent) by the end of 2007.

The second proposed rule establishes “standards of performance” limiting mercury emissions from new and existing utilities. This proposal, under section 111 of the Clean Air Act, would create a market based “cap-and-trade” program that, if implemented, would reduce nationwide utility emissions of mercury in two distinct phases. In the first phase, due by 2010, emissions will be reduced by taking advantage “co-benefit” controls - that is mercury reductions achieved by reducing SO₂, and NO_x emissions. When fully implemented, mercury emissions will be reduced by 33 tons (69 percent).

New regulations, along with rules already in place or anticipated for control of nitrogen oxides, sulfur dioxide and particulate matter, make clear the need for a multi-pollutant control technology—one that keeps coal-fired power generation, the single largest source of electrical energy in the U.S., a viable and economical component of the generating portfolio. To this end Powerspan Corp. conducted pilot scale testing of a multi-pollutant control system in cooperation with FirstEnergy Corporation (Akron, OH) at FirstEnergy's Burger Power Plant.

It is Powerspan's objective to develop and demonstrate an integrated, cost-effective air pollution control technology for coal-fired power plants that achieves major reductions in emissions of nitrogen oxides (NO_x), sulfur dioxide (SO₂), particulate matter (PM), mercury (Hg), and other air toxic compounds. Another goal of the technology is to maximize by-product utilization, minimize use of reagents, and minimize generation of solid and liquid

wastes. In pursuit of these objectives, Powerspan pilot tested an innovative, patented process to simultaneously remove NO_x, SO₂, fine PM, and mercury from the exhaust gas of coal-fired power plants.

1.2 ECO Technology Overview

The ECO (Electro-catalytic Oxidation) system is a four-stage pollution control process that integrates several technologies to remove high levels of the primary air pollutants generated by coal-fired power plants. The four stages of ECO technology are:

Stage 1: A dielectric barrier discharge reactor that oxidizes NO and Hg

Stage 2: An absorber that removes SO₂ and NO₂

Stage 3: A wet electrostatic precipitator used to collect aerosols and fine particles

Stage 4: A coproduct treatment system for removal of Hg and ash from the liquid co-product stream prior to producing solid commercial grade fertilizer

A more complete description of each one of the ECO stages is given below.

Stage 1: ECO Reactor - Oxidation of pollutants

A dielectric barrier discharge (DBD) reactor is used to initiate the ECO process chemistry. It is accomplished through generation of a non-thermal plasma in which energetic electrons (~5 eV) create radicals leading to pollutant oxidation. The electron energies formed in the barrier discharge are ideal for generating gas-phase radicals, such as hydroxyl (OH) and atomic oxygen (O). Formation occurs through collision of electrons with water and oxygen molecules present in the flue gas.

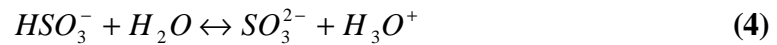
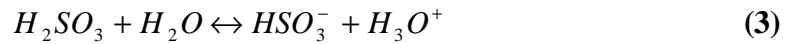
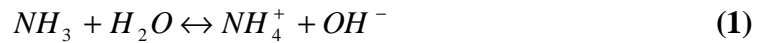
The dielectric barrier discharge reactors used in the ECO process are similar to gas reactors used in large industrial ozonators for water purification and disinfection. In a flue gas stream, these radicals oxidize NO_x, SO₂ and Hg to form NO₂, nitric acid (HNO₃), sulfuric acid (H₂SO₄) and mercuric oxide (HgO) respectively. Further details of

the DBD reactor operation as part of the ECO process are discussed in section 2.0 of this technical report.

Stage 2: Scrubber - *Collection of SO₂ and NO₂*

An ammonia scrubber is used in the ECO process in order to achieve high removal efficiencies of NO_x and SO₂ while reducing the power requirements of the barrier discharge reactor. Flue gas entering the scrubber is first quenched to saturation. The gas then enters a scrubbing stage, which captures both SO₂ and NO₂. Ammonia is utilized in order to scrub SO₂ at a high rate and to produce compounds capable of reducing NO₂ to nitrogen. Ammonia also neutralizes the acids (HNO₃ and H₂SO₄) created in the barrier discharge reactor and produce ammonium sulfate and nitrate, a useful fertilizer byproduct, from the acids and scrubbed SO₂. The synergy between SO₂ scrubbing and capture of NO₂ produced from NO_x in the barrier discharge reactor results in a system with the ability to achieve high levels of NO_x and SO₂ removal.

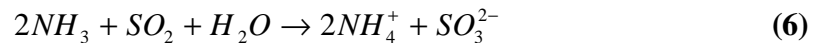
The scrubbing chemistry starts with ammonia in aqueous solutions producing ammonium and hydroxyl (base) ions as shown in reaction (1). Reactions (2) through (4) show the absorption of SO₂ into aqueous solution producing sulfurous acid (H₂SO₃), bisulfite (HSO₃⁻), sulfite (SO₃²⁻) and hydronium (H₃O⁺) ions.



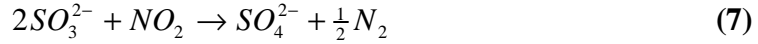
The hydroxyl and hydronium ions react to maintain a neutral pH, driving the SO₂ absorption reactions (2) through (4) to produce sulfite.



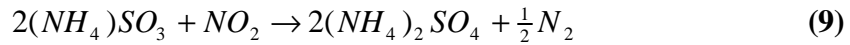
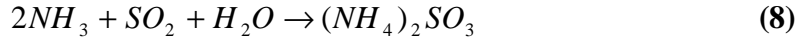
Combining reactions (1) through (4) yields the overall SO₂ scrubbing reaction (6)



Sulfite produced by reaction (6) reacts with NO₂ through oxidation-reduction reaction (7) reducing NO₂ to nitrogen while oxidizing sulfite to sulfate:



From reactions (3) through (7) the overall reactions for SO₂ and NO₂ scrubbing with ammonia can be written as:



The ratio of SO₃²⁻ to HSO₃⁻ in solution (4) is determined by solution pH. Both compounds are reported to scrub NO₂, but the rate of reaction between NO₂ and SO₃²⁻ is reported to be forty times faster than that of NO₂ with HSO₃⁻. [1] Therefore, pH control of the scrubbing solution through addition of ammonia is essential to ensure that an adequate SO₃²⁻ concentration is maintained for high NO₂ scrubbing rates. From reactions (8) and (9) it can be seen that a minimum of two moles of SO₂ are required for each mole of NO₂ reduced to N₂. However, the sulfite needed for NO₂ reduction can also be consumed by O₂ in the flue gas, effectively increasing the ratio of SO₂ to NO₂ required for NO₂ scrubbing:



Oxidation of sulfite to sulfate results in a minimum ratio of SO₂ to NO_x of 3 in order to maintain a sulfite concentration adequate to scrub NO₂ to acceptable levels.

Compounds produced in the scrubbing of SO₂ and NO₂, can also result in the reduction of oxidized mercury (Hg²⁺) to elemental mercury (Hg⁰), reversing the oxidation process accomplished by the barrier discharge reactor. Understanding the extent to which the reduction reactions occur and, if necessary, developing a means to retard the reaction was a focus of laboratory investigation and the pilot test program. Solutions to the problem of mercury reduction included altering the conditions of the scrubber chemistry to retard the rate of reduction and treatment of the scrubber solution to remove mercury. The treatment process must keep the steady state mercury concentration low enough to substantially diminish the rate of mercury reduction.

Stage 3: Wet ESP - Collection of acid aerosols and fine particles

Flue gas exiting the ammonia scrubber contains oxidized mercury and fine particulate matter. It will also contain aerosols generated in the barrier discharge and ammonia scrubbing process steps (NH_4HSO_4 , NH_4NO_3 , NH_4Cl). These materials are captured in a wet electrostatic precipitator (WESP) and returned to the scrubbing solution. A WESP is efficient at collection of aerosols and fine particulate matter since there is no mechanism to cause re-entrainment. In a WESP, liquid flows down the collecting plate to remove captured materials from the plate. The advantages of WESPs include: a) water flow prevents particle re-entrainment, which would limit collection efficiency; b) the water layer does not limit corona current; and c) the improved collection characteristics permit high gas velocities, limiting the equipment size required for collection.

Stage 4: Co-Product Treatment System - Production of commercial-grade fertilizer

Ammonium sulfate and nitrate created in the ECO process can be treated and used as a commercial fertilizer. Solids in the scrubber bleed stream, consisting of ash and insoluble metal compounds, are removed by filtration. The stream is then pumped through an activated carbon adsorption bed. The activated carbon used in ECO is produced by Nucon International (Columbus, OH) and sold under the name of Mersorb[®]. The mercury reacts with the sulfur impregnated activated carbon and is retained in the adsorbent bed while the liquid continues through processing.

Liquid substantially free of mercury and ash can be used directly or sent to a crystallizer in which moisture is driven off to produce crystals of well-defined size, strength, and composition. The crystals may be usable as fertilizer in the form produced by the crystallizer, or may be processed to further reduce the moisture of the crystals or to agglomerate the crystals into granules. Spent mercury-laden activated carbon is replaced and disposed of as a hazardous waste. It is estimated that the variable cost of mercury removal with activated carbon is \$733 per pound of mercury, including the media and disposal.

The co-product treatment system uses standard fertilizer crystallization and granulation processes and equipment. All processing can be done on-site, or the crystalline material can be generated on site and then shipped to a fertilizer processing plant.

2.0 Description of Reactor Operations in the ECO Process

The dielectric barrier discharge reactor initiates the ECO process chemistry through oxidation of gaseous pollutants in the flue gas. To form a barrier discharge, a dielectric insulating material is placed between two discharge electrodes. Typically, the material has a high dielectric strength and high dielectric constant (e.g., glass or ceramic) and covers one of the two electrodes. High voltage applied to the electrodes causes the gas in the gap to breakdown. Presence of the dielectric barrier prevents this breakdown from forming an arc with its resulting high energy consumption. Instead, breakdown is in an array of thin filament current pulses, or “microdischarges.” They are well distributed spatially over the discharge gap. Typical duration of a microdischarge is of the order of a few nanoseconds, and electron energies range from 1 to 10 electron volts.

The electron energies formed in the microdischarge are ideal for generating gas-phase radicals, such as hydroxyl (OH) and atomic oxygen (O) through collision of electrons with water and oxygen molecules present in the flue gas stream as shown in reactions (11) through (13) below:



In a flue gas stream, these radicals simultaneously oxidize Hg, NO_x, and SO₂ to form mercuric oxide (HgO), nitric acid (HNO₃) and nitrogen dioxide (NO₂), and sulfuric acid (H₂SO₄), respectively [2]. Simplified reaction paths are presented below.



All of the above reactions can be made to occur at low temperature (150-300°F). Additional reactions leading to the production of acids, such as oxidation of SO₂ by O atoms, are also initiated by the discharge. References have been included for more information on dielectric discharge processing [3,4,5] of NO_x and the combined barrier discharge processing [6,7,8,9] of NO_x and SO₂ in a flue gas stream.

Presence of a dielectric barrier allows for several possible electrode configurations, including coaxial cylinders, cylindrical electrodes with plates, and parallel plate electrodes. Different reactor configurations have little effect on overall conversion efficiency [10,11]. This allows establishing electrode spacing that reduces the potential for plugging of the reactor and results in a minimal pressure drop across the reactor.

The reactor for the ECO Pilot at the Burger Power Plant used for testing elemental mercury oxidation is shown in

Figure 1. The inset picture in the right hand corner of the Figure shows the discharge looking down one electrode in the DBD reactor. The purple glow is due to the interaction of electrons with nitrogen, the predominant species in the gas. The power supply is capable of supplying 100 kW of power into the flue gas and works in conjunction with the power supply to allow the unit to continue operation if one of the 143 fused electrodes fails.

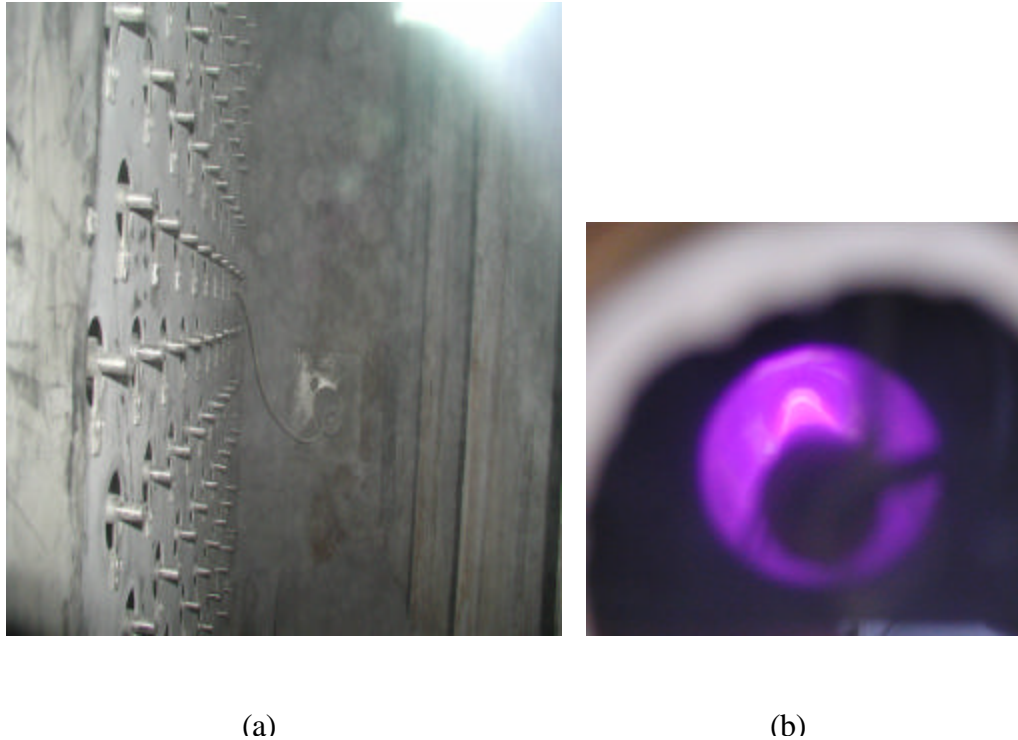


Figure 1: (a) ECO Pilot DBD Reactor at the R.E. Burger Generating Station, (b) Discharge looking down the center of one tube

Although the actual conversion varies with inlet conditions, Figure 2 below shows the typical behavior of NO and SO₂ in Powerspan's barrier discharge reactor as a function of the electrical energy supplied to the reactor. The inlet NO_x concentration for this data is 0.4 lb/MMBtu. NO conversion shown in the figure is the portion of flue gas NO converted to either NO₂ or HNO₃. The curve labeled NO_x conversion represents the portion of NO converted to HNO₃, so that the difference between NO and NO_x conversion is the percentage of incoming NO converted to NO₂. SO₂ conversion represents the percentage of flue gas SO₂ converted to SO₃ and H₂SO₄.

In addition to oxidation of NO and SO₂, the DBD reactor oxidizes elemental Hg. Elemental mercury has a low solubility in aqueous solutions, making it difficult to remove from flue gas streams. On the other hand, it has been repeatedly shown by FGD systems that oxidized mercury can be captured by scrubber solutions because of its increased solubility. Therefore, oxidizing elemental mercury in the flue gas stream

increases the Hg removal ability of scrubbers. Oxidized mercury will pass through the DBD reactor unaffected.

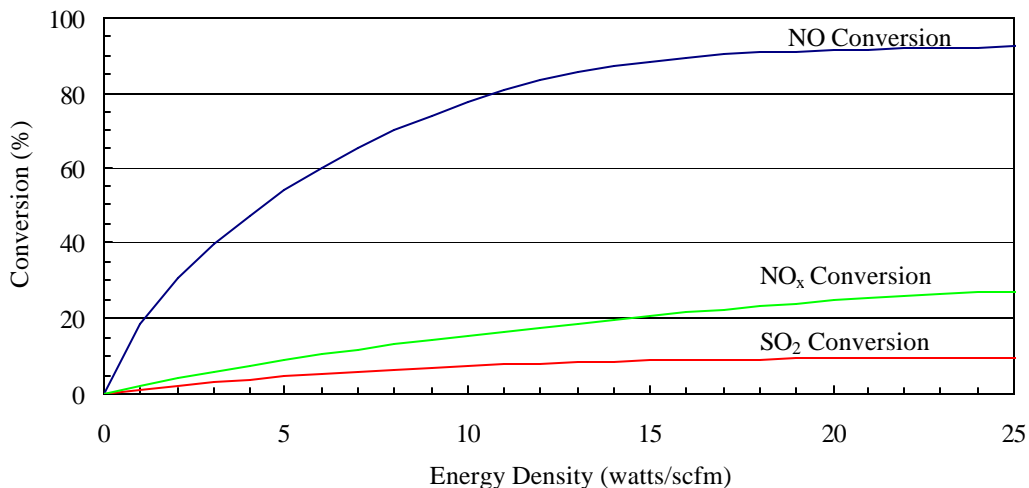


Figure 2: Dielectric Barrier Discharge Conversion for 0.4 lbm/MMBtu Inlet NO_x

2.1 ECO Pilot Overview

The ECO pilot system, constructed at FirstEnergy's Burger Power Plant, was in operation for four years prior to this cooperation agreement with DOE to support development of the ECO technology. It was modified at the beginning of 2002 to incorporate the ammonia based NO₂ and SO₂ scrubber and its associated liquid handling equipment. A decision was made prior to the modification to keep the unit in a horizontal configuration, as opposed to the vertical configuration to be commercially deployed. The decision was based on a desire to minimize the time required to complete modifications and investigations of the process chemistry in actual flue gas.

The pilot, in its initial configuration, drew a slipstream of gas from the Burger Plant's Unit 4 or 5, upstream of the unit's ESP. The gas was returned to the unit at the Burger plant ESP inlet. Gas flow into the pilot, at a rate of 1500 to 3000 scfm (standard cubic feet per minute), passed through a small cyclone separator and two dry ESP fields,

each four feet in length. These two units in series were used to try to reduce the ash content of the flue gas to a level similar to that expected after a plant's ESP or fabric filter, which would be the location for full-scale ECO installations. The configuration is illustrated in Figure 3 below.

Upon exiting the Powerspan dry ESP, flue gas entered a multi-tube, coaxial cylinder barrier discharge reactor. High voltage applied to the center electrodes of the discharge reactor created the non-thermal plasma that formed radicals leading to oxidation of gaseous pollutants. The ECO pilot reactor was capable of delivering up to 100 KW of electrical discharge energy to the gas.

The ammonia scrubber followed the barrier discharge reactor and was in an absorber vessel consisting of three packed sections in a cross flow configuration. The first section cooled and saturated the flue gas. It was four feet deep in the direction of gas flow. Next was a six-foot scrubbing section to remove SO₂ and NO₂. Following the scrubbing section was a six-inch packed section that absorbed gaseous ammonia exiting the scrubbing section.

Gas exiting the absorber vessel entered a horizontal, three-field WESP. Each field was thirty inches deep in the unit of gas flow. The collecting plates were washed periodically, and the liquid effluent was sent back to the ammonia scrubber section.

Due to excessive ash loading through the ECO system and the subsequent problems that were introduced, the configuration of the pilot was changed such that the slipstream of flue gas was drawn from downstream of the Burger plant's Unit 4 dry electrostatic precipitators. After this configuration change, the cyclone separator was removed from the gas path and the pilots' dry electrostatic precipitator fields were shut off to make the pilot flue gas representative of what would be seen in a commercially deployed ECO installation. This pilot slipstream configuration change was implemented in July of 2003 and run until December 2003.

A seven-man crew operated the Burger pilot on a three shifts per day basis. Continuous emissions monitoring was accomplished at the flue gas inlet to and exit from the pilot. The system measured the concentration of SO₂, NO_x, O₂, H₂O, CO₂, CO and NH₃. Outlet flue gas flow and opacity were also measured continuously. Temperatures, flow rates, pH of all liquid flow streams, and pressure drop across all process units were

also measured. Mercury concentration in the pilot flue gas was measured using PS Analytical's Sir Galahad semi-continuous mercury CEM systems. Two systems were installed to provide simultaneous, near real time measurement at the pilot inlet and outlet as well as at other selected locations. The systems reported elemental and total gas phase mercury concentrations and are discussed later in this report. In all, over 175 parameters were continuously recorded by automatic data logging equipment.

ECO™ Pilot Unit at FirstEnergy's R.E. Burger Plant

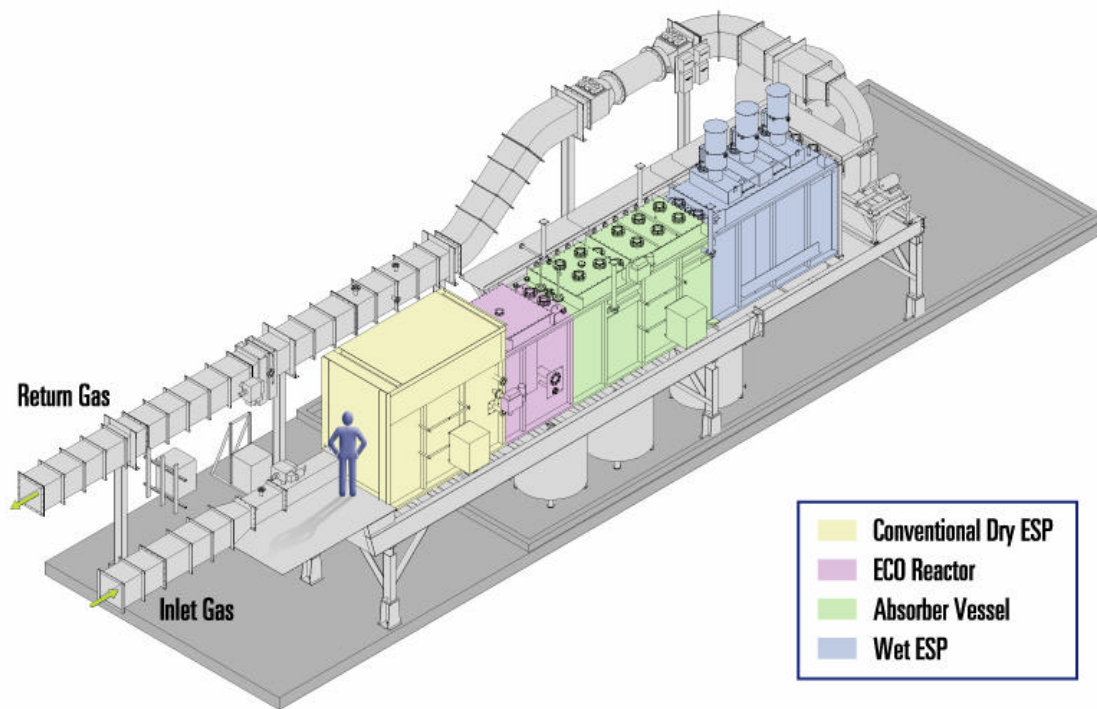


Figure 3: Layout of the ECO Pilot at FirstEnergy's Burger Plant

The coal burned at FirstEnergy's Burger Power Plant is typically a blend of eastern bituminous and subbituminous coal. The blend varies during normal operation and produces a high percentage of oxidized mercury compared to elemental mercury in the flue gas and a reactive ash.

3.0 Elemental Mercury Injection

The typical mercury concentration in the flue gas at FirstEnergy's Burger Power Plant contains a low percentage of its total mercury emissions as elemental Hg. As described in a separate task report, Air Compliance Testing performed Ontario Hydro testing during May 8-10, 2002. Table 1 lists the results from Ontario Hydro Testing of the flue gas at the inlet of the ECO process. The results show the elemental Hg fraction is <3% of the total mercury in the flue gas stream.

Hg Fraction	Concentration ($\mu\text{g}/\text{Nm}^3$)
Particle Bound Hg	0.62
Oxidized Hg	5.81
Elemental Hg	0.16
Total Hg	6.59

Table 1: Results from Ontario Hydro testing of the flue gas at the ECO pilot inlet.

To effectively demonstrate the ability of the ECO DBD Reactor to oxidize elemental mercury, its concentration was artificially raised through the addition of elemental mercury to the flue gas stream. The mercury addition system used is shown in Figure 4 below

Elemental mercury is added to the flue gas stream with the above addition system by saturating a stream of air with mercury. The saturation is controlled by air flow and the temperature of the mercury condensation vessels. Elemental mercury is vaporized in a mercury evaporation vessel and swept out by the air passing through the vessel. The mercury laden then enters a series of four vessels in a controlled temperature bath. The gas residence time in the condensing vessels ensures that the gas stream is saturated with mercury at the temperature of the condensing temperature bath. The mercury evaporation vessel temperature is set to ensure that the mercury content of the gas leaving.

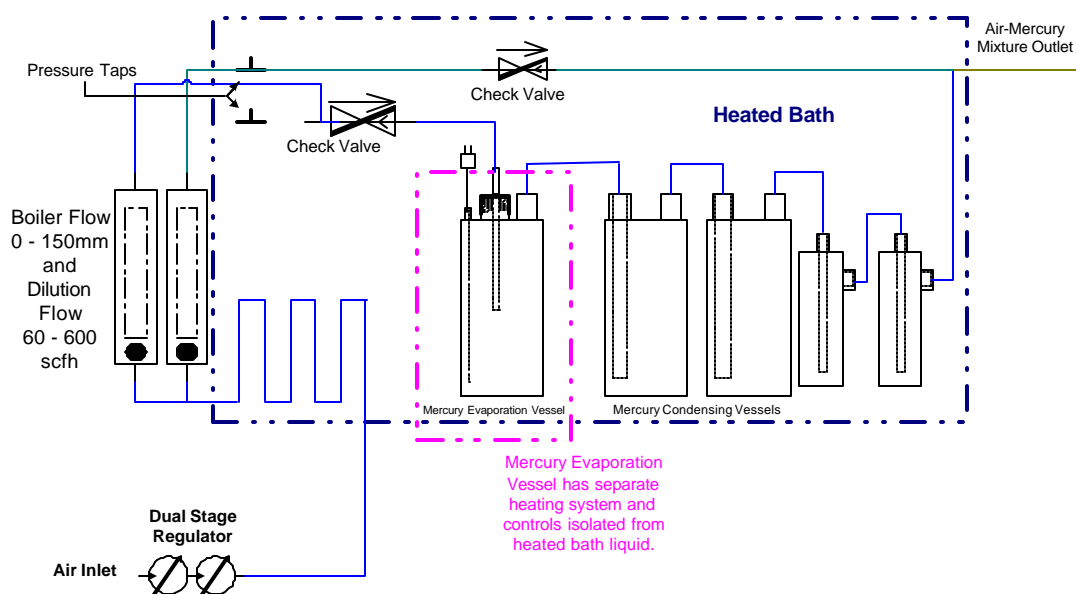


Figure 4: Schematic of the system used to inject elemental mercury into the flue gas.

the evaporation vessel is greater than the saturation content for the condensing vessel temperature. Since the air/Hg stream exiting the condensing vessels is above saturation for ambient temperature, the stream is diluted prior to leaving the temperature controlled environment of the addition system to eliminate the need to heat trace the addition line to the injection point.

Figure 5 shows the results of adding elemental Hg to the flue gas stream. The flue gas was taken from the inlet of the Burger Power Plant ESP. The expected concentration of Hg(0) was $60 \mu\text{g}/\text{Nm}^3$. The actual concentrations that were seen were only $\sim 26 \mu\text{g}/\text{Nm}^3$ of total Hg and $\sim 6.0 \mu\text{g}/\text{Nm}^3$ of elemental Hg. This represents a recovery of 10% as elemental mercury out of the total mercury added to the flue gas stream. Only 37% of the total mercury added was recovered. The oxidation of the added elemental mercury is attributed to the fly ash in the flue gas stream. Since the flue gas was taken prior to the plant's ESP, and the ash removal devices used for the ECO pilot were not as effective as the plant's ESP, the ash loading was approximately 10 times what is expected on the outlet of the ESP. The combination of the amount of ash and its

reactive nature significantly complicated the effort to increase the concentration of elemental mercury for testing oxidation of the elemental mercury in the DBD reactor.

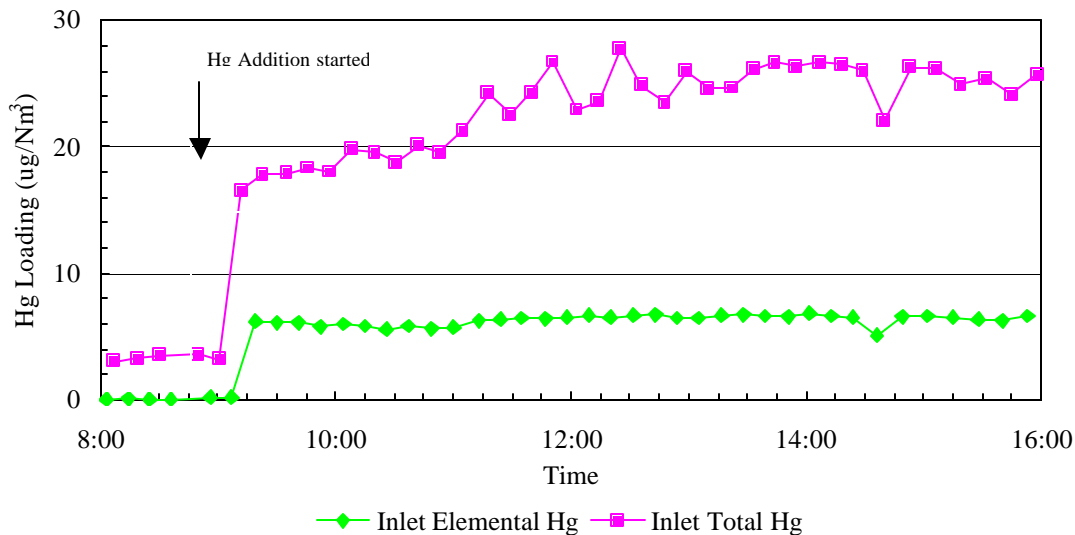


Figure 5 : Addition of elemental mercury vapor to the flue gas

3.1 Ash Effects on Elemental Mercury

Clearly, the reactive ash at the R.E. Burger Power Plant could effect the measurement and speciation of mercury. It was also shown in Figure 5 that the ash reacted with injected elemental Hg, decreasing the yield of gas phase mercury, both elemental and oxidized that could be obtained with the addition system. Further investigations were done looking at the ash loading of the system and how it compared to conditions that are expected in a typical installation, such as at the outlet of the Burger Plant's ESP.

Ash loading measurements were made at the inlet of the ECO system and compared to the Burger Plant's reported ash loading on the outlet of the ESP. The results are shown in Figure 6; the red line is the measured ash loading on the outlet of the Burger Plant's ESP; the green triangles represent testing that show what was measured by Air Compliance Testing at the inlet of the ECO process using Method 5: (Determination of Particulate Matter Emissions from Stationary Sources), and the blue line shows the

results of measurements made by Powerspan using an ash sampler at the inlet of the ECO process. The Powerspan ash sampler reports low compared to the Air Compliance Testing results obtained at the same time. However, the Powerspan Ash Sampler was designed only to give an indication of the day-to-day variations in ash loading at the inlet of the ECO pilot rather than as an isokinetic sampling system. The measurements show that the ash loading is consistently and substantially higher at the inlet of the ECO system than is present at the outlet of the Burger Plant dry electrostatic precipitator. The high ash loading is the likely cause of oxidation of Hg from the elemental Hg addition system and of contamination and speciation problems with the Hg sample probes.

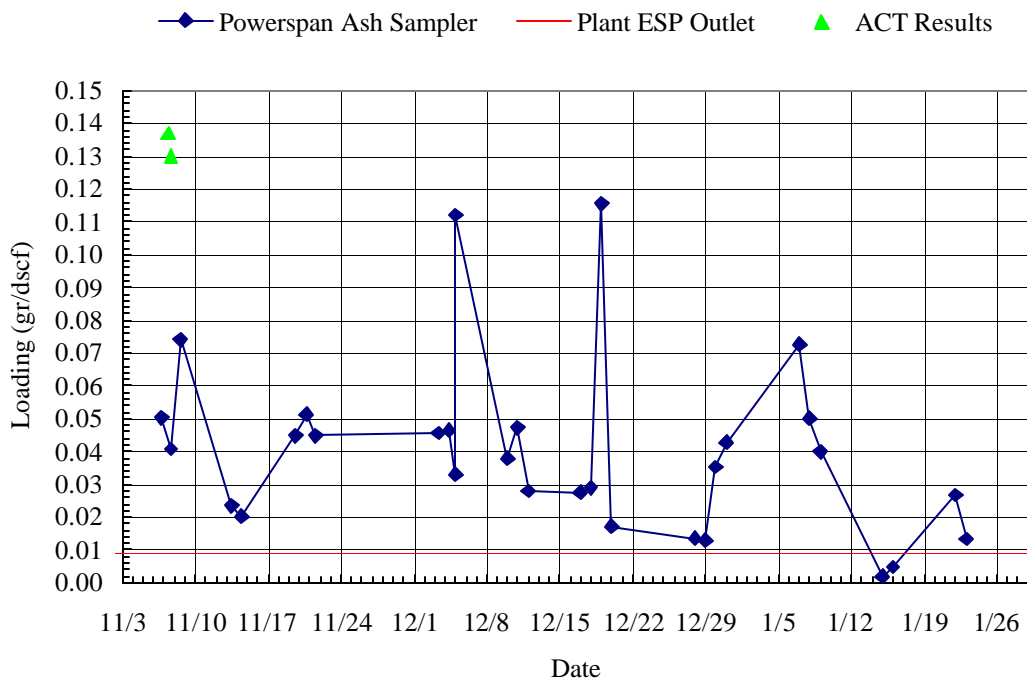


Figure 6: Ash loading measurements made at the ECO system inlet.

Due to the difficulty of operating in the high ash environment and the inability to adequately verify the ability of the reactor to oxidize elemental Hg, Powerspan invested in a new duct configuration that supplied flue gas from the outlet of the Burger plant precipitator rather than the inlet in order to decrease the ash loading and facilitate testing of the reactor.

With the new duct in place, the ability to add elemental Hg was again tested. The results are shown in Figure 7. For this testing, two elemental Hg levels were chosen.

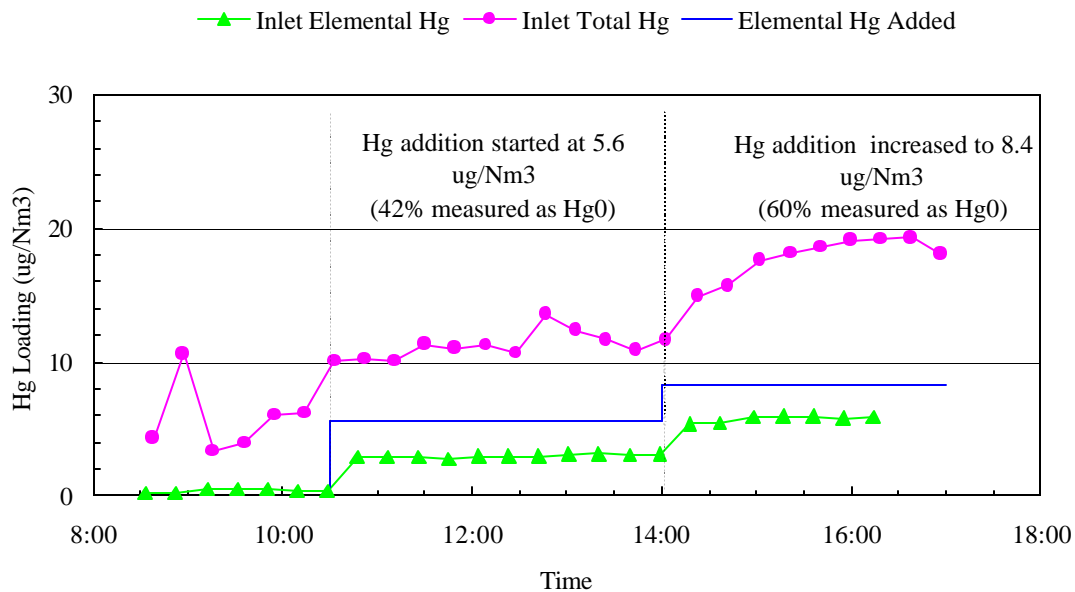


Figure 7: Recovery of Hg⁰ after the new duct installation on the outlet of the ESP.

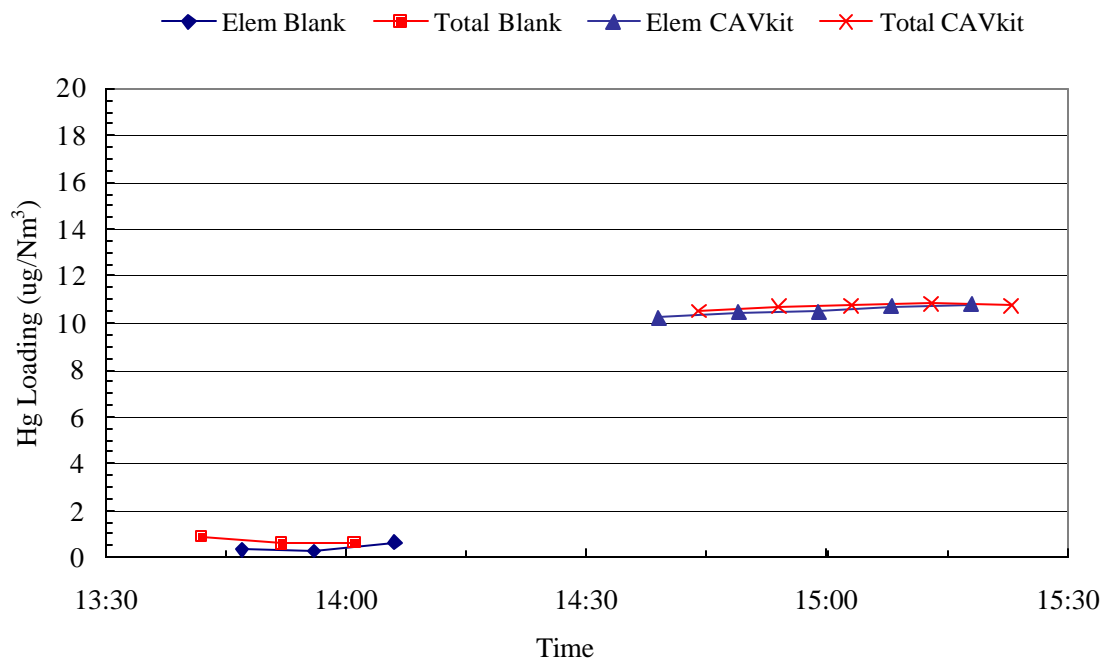


Figure 8: Results of inlet blanks and CAVkits run on a clean QGIS filter.

The first was an addition of $5.6 \mu\text{g}/\text{Nm}^3$ of elemental Hg. The blue line in the figure represents the expected $\text{Hg}(0)$ concentration, and the green line represents the amount of elemental mercury actually measured. At this level, 42% of the added mercury reported as elemental mercury and 100% of the added mercury was recovered. The second test shows an increased level of addition to the flue gas with $8.4 \mu\text{g}/\text{Nm}^3 \text{Hg}^0$ concentration expected. The measured concentration shows that in this case 60% of the mercury added reported as elemental Hg and again 100% of the Hg added was measured.

By reducing the ash loading on the system, it was possible to add elemental Hg to the flue gas at a level where meaningful testing could be performed to investigate the oxidation of elemental Hg in the reactor.

Even with the decreased ash loading in the ECO inlet, repeated QA/QC measurements through the inlet mercury sampling system indicated that within several days of continuous use, oxidation of elemental mercury was observed to occur across the QGIS filter. Figure 8 illustrates QA/QC data obtained when the QGIS filter was in a clean and uncontaminated condition. An analysis indicates that only 1.6% of the injected elemental mercury was lost across the entire sampling system, including the QGIS filter. After using the filter for approximately 80 hours to sample flue gas at the ECO inlet location, the same QA/QC protocols were run. The results in Figure 9 show a 25 % bias towards oxidized mercury, even though only elemental mercury was injected upstream of the filter.

In an effort to reduce the oxidation of elemental mercury across the QGIS filter, personnel at Apogee Scientific suggested a series of protocols for cleaning the filter. These protocols, discussed in a separate task report, were initially successful in keeping the oxidation of elemental mercury across this filter to a minimum. However, after running the QGIS probe over a number of weeks, the cleaning protocols became permanently ineffective. After this point, unacceptable amounts of elemental mercury oxidation across the QGIS filter were always observed to occur. These amounts varied from 25% to as much as 60% of the injected elemental mercury vapor. The inability to adequately clean the QGIS filter after prolonged use was observed for two filter elements and is considered to be a likely performance characteristic of these filters.

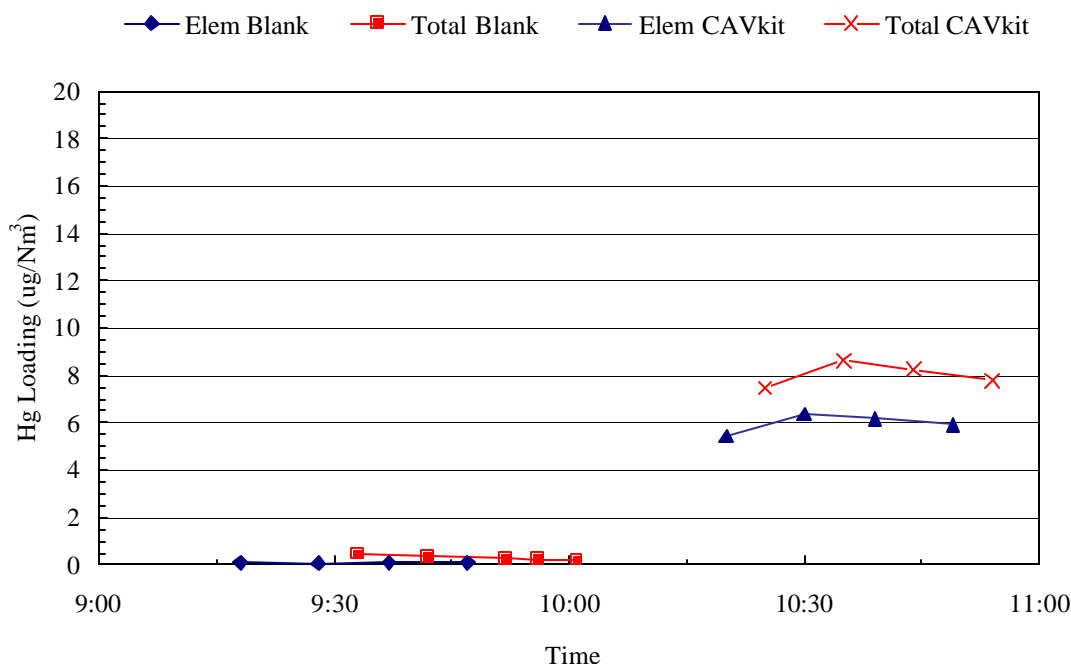


Figure 9: Results of blanks and CAVkit runs on a QSiS filter after ~80 hours of use

3.2 Mercury Measurements and Sampling

Measuring changes of elemental mercury across the reactor were hampered by the reactive ash described above as well as by instrumentation issues described in detail in a separate technical report. Briefly, sample extraction, ash contamination, and hardware failures allowed the instruments to run for only short periods of time before maintenance was required. In addition, the inlet sampling system would not obtain quality data for a long enough period to be able to complete a series of tests. Although it would have been ideal to take measurements directly on the outlet of the reactor, the sample conditioning required to remove the acid mists produced by the reactor to avoid damaging equipment was prohibitive.

Therefore, all measurements to verify reactor performance were made using the sample probe on the ECO system outlet, which is after removal of ash by the pilot's wet electrostatic precipitator. The elemental mercury concentration was monitored while the

reactor power was cycled on and off at the desired energy density. More specifically, the reactor was run for one to two hours while mercury measurements were made. After several cycles of elemental and total mercury measurements, the reactor was shut off to obtain elemental and total mercury concentrations. Without the reactor on, there is no mechanism to remove elemental mercury from the process and therefore the elemental mercury concentration at the outlet of the system is representative of the inlet mercury levels once corrected for dilution and air in-leakage. Sampling on the outlet of the system eliminates oxidation of mercury by reactive ash on the sample filter while still providing the information required to evaluate the ability of the DBD to oxidize elemental mercury. The results of the reactor testing are discussed in section 4.0.

4.0 Reactor Testing and Results

Testing of the barrier discharge reactor's ability to oxidize elemental mercury was performed using two flue gas configurations. The first configuration was one in which flue gas was supplied to the ECO pilot from the pilot inlet to the Burger plant's ESP and utilized the pilot's cyclone separator and dry ESP for ash removal. In this configuration, the ash loading on the ECO reactor was measured to be 0.13 gr/dscf. In the second configuration, after installation of new ductwork, flue gas was supplied from the outlet of the Burger plant's ESP, substantially reducing the ash loading on the ECO pilot. Measurements of the ash loading at the outlet of the Burger plant ESP showed an average ash loading of 0.009 gr/dscf.

Testing of elemental mercury oxidation by the barrier discharge reactor was performed using elemental mercury injection into the inlet flue gas duct and mercury measurements at the outlet of the ECO system only. Inlet elemental mercury measurements could not be reliably made due to the sampling difficulties encountered as a result of ash contamination of the sample system at the inlet to the pilot. Sampling efforts at the ECO pilot inlet are discussed briefly in this report (section 3.2) and in more detail in a separate task report.

Shown in Figure 10 are results from testing where the DBD reactor was operated at a power level of 18 w/scfm and the flue gas flow through the ECO pilot was held at 1500 scfm with an inlet elemental Hg concentration determined to be ~2.5

ug/Nm³. The inlet elemental mercury concentration was taken to be that measured at the outlet of the system with the DBD reactor secured. Measurements at the outlet with and without the DBD reactor operating show the oxidation of elemental Hg by operation of the DBD.

At the completion of these tests, the amount of elemental mercury injected into the ECO inlet duct was increased and the reactor on/off sequence was performed again. The data from these tests are presented below in Figure 11.

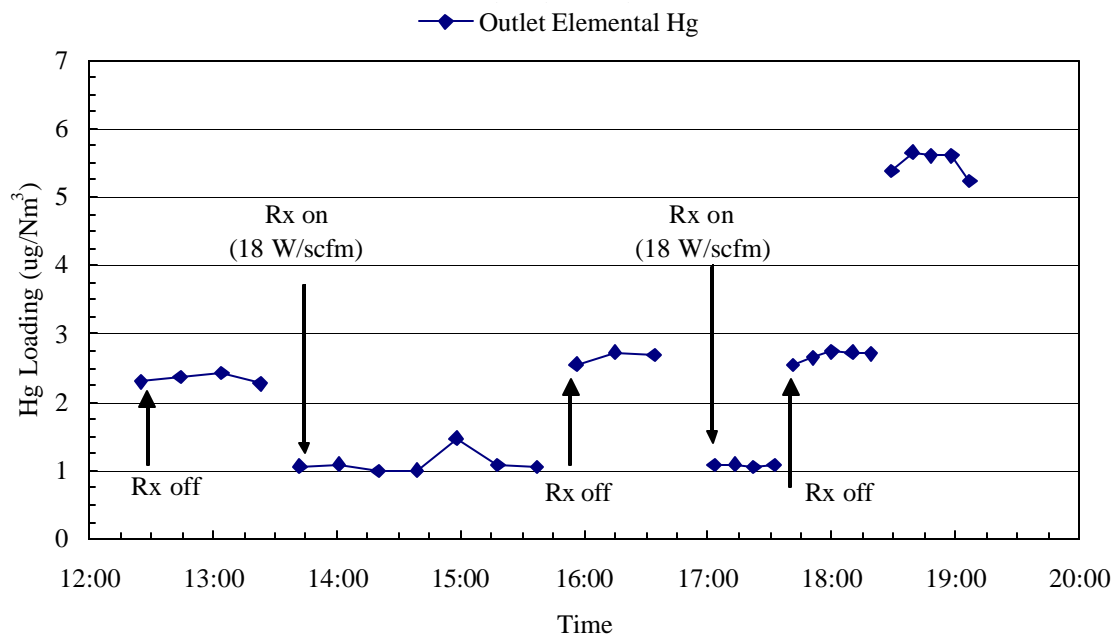


Figure 10: ECO DBD reactor performance in high ash loading environment

The results of elemental mercury oxidation by the barrier discharge reactor in the high reactor inlet ash loading configuration are summarized above in Table 2. The reported inlet elemental Hg concentration is the average concentration measured at the outlet of the system with the DBD reactor secured.

The reactor testing was repeated after installation of a new duct run, connecting the ECO pilot to the Burger Plant dry ESP outlet. This correlation is referred to as “normal ash loading” because it represents ash loading expected in a commercial installation.

Installation of the new duct was intended to alleviate the problems encountered with injection and measurement of elemental Hg at the inlet to the ECO

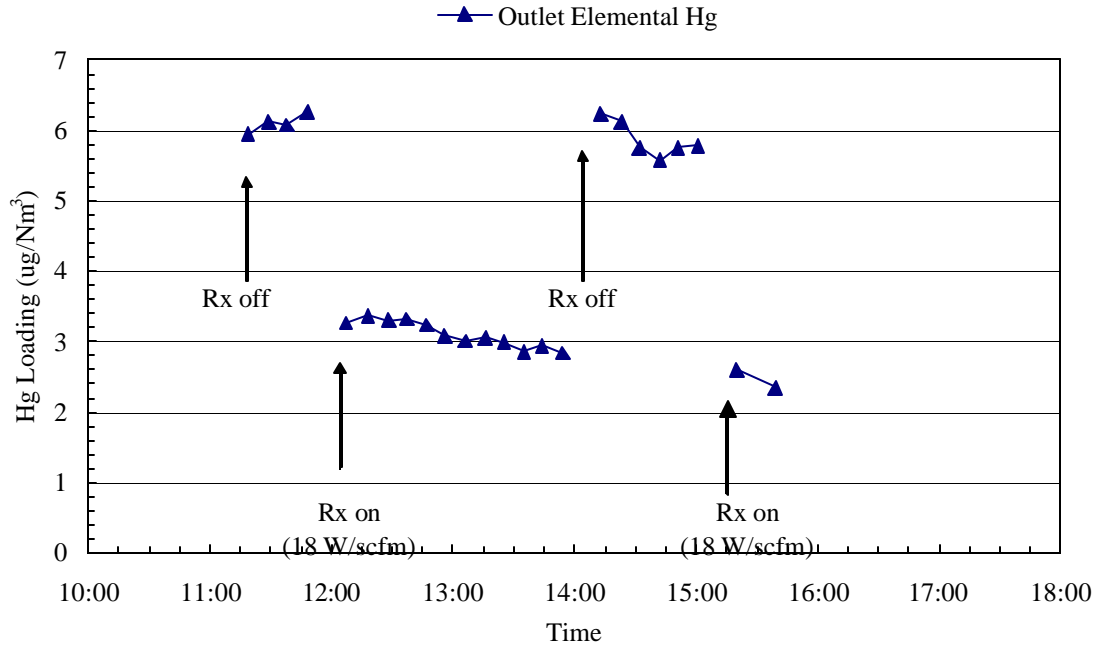


Figure 11: Conversion of elemental mercury at 18 watts/scfm at higher concentration with high ash loading

Run	DBD Reactor Inlet Elemental Hg ($\mu\text{g}/\text{Nm}^3$)	DBD Reactor Outlet Elemental Hg ($\mu\text{g}/\text{Nm}^3$)	Elemental Hg Conversion.
1	2.3	1.1	53%
2	2.7	1.1	60%
3	6.1	3.1	49%
4	5.9	2.5	58%

Table 2: Elemental Hg conversion at 18 W/scfm, 1500 scfm gas flow

pilot. Although much reduced, some oxidation of elemental Hg continued to take place in the sampling system and inlet ductwork. Therefore testing was conducted as in the initial duct configuration where the inlet concentration was taken to be that measured at the outlet of the pilot with the DBD reactor secured. The tests were conducted at two flowrates: 2000 scfm and 2500 scfm. During each of these runs the DBD reactor was

cycled between 0, 15, 20 and 25 Watts/scfm. The results from the low flow tests are presented below in Figure 12. Based on calibration of the mercury addition system, the concentration of elemental mercury injected into the duct during these tests was $8.7 \mu\text{g}/\text{Nm}^3$.

The results from the high flow (2500 scfm) tests are presented below in Figure 13. The result of increasing the reactor power density is also visible in the data. We calculated that the amount of elemental mercury injected into the duct during the high flow tests was $7.5 \mu\text{g}/\text{Nm}^3$. The results of both high and low flow test as a function of reactor power are summarized below in Table 3.

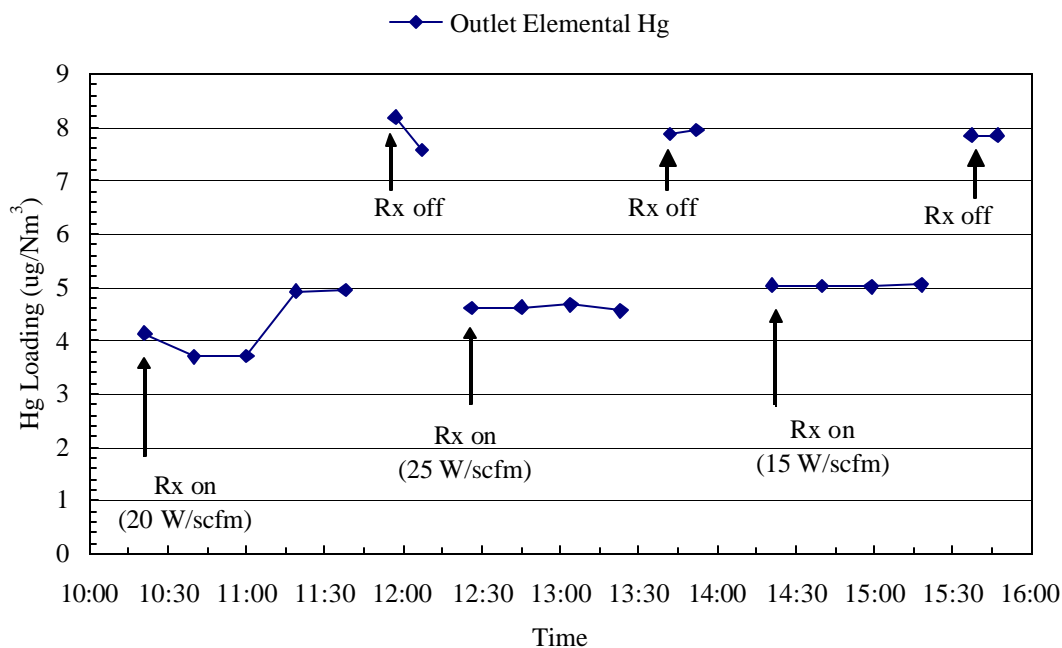


Figure 12: Elemental mercury conversion at 20, 25 and 15 W/scfm with normal ash loading at a flow rate of 2000 scfm, Runs 1,2 and 3

A plot of elemental Hg oxidation as a function of reactor power density, for both the high and low flow tests is presented below in Figure 14. The figure shows an increase in elemental Hg oxidation as a result of increasing DBD reactor power.

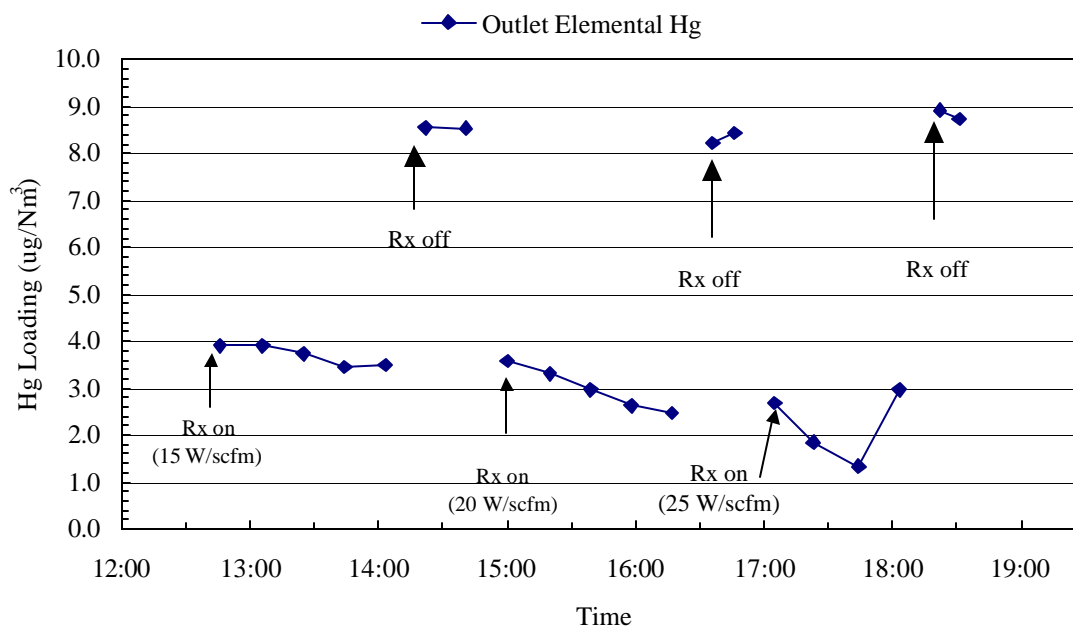


Figure 13: Elemental mercury conversion at 15, 20 and 25 W/scfm with normal ash loading at a flow rate of 2500 scfm, Runs 4,5 and 6.

Run	Rx Power Density (W/scfm)	Flue Gas Flow (scfm)	Elemental Hg Conversion
1	15	2000	36%
2	20	2000	46%
3	25	2000	42%
4	15	2500	57%
5	20	2500	64%
6	25	2500	75%

Table 3 Elemental Hg conversion at 15, 20 and 25 W/scfm at two different flue gas flow rates.

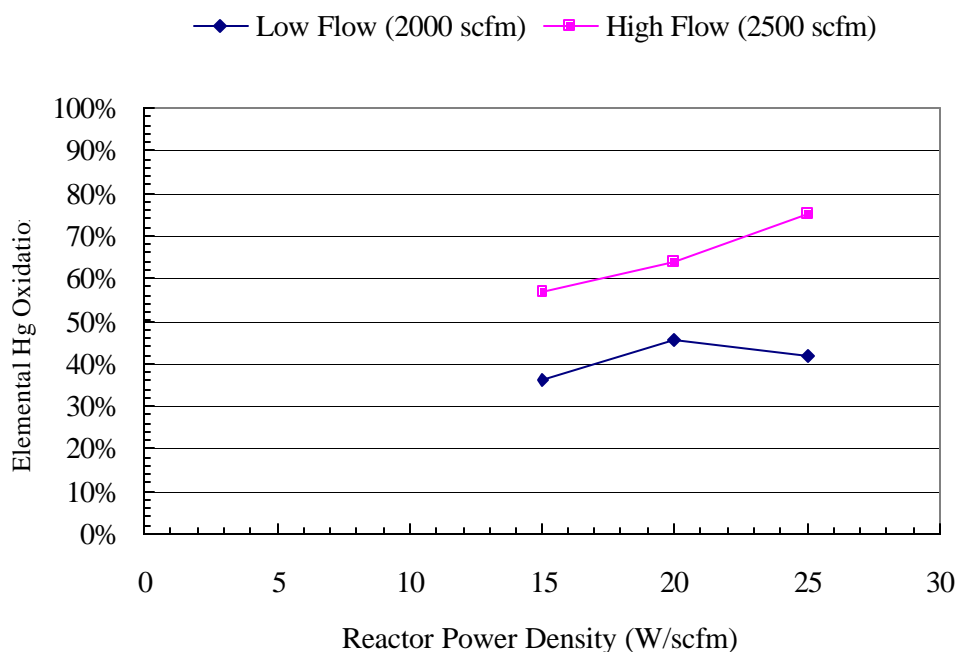


Figure 14: Elemental Hg conversion at 15, 20 and 25 W/scfm at two different flue gas flow rates.

5.0 Discussion

The investigation of elemental Hg oxidation by the DBD reactor in the ECO process was severely hampered by the inability to artificially raise and accurately measure the elemental Hg concentration in the pilot inlet flue gas. The natural elemental Hg concentration measured at the Burger Plant is typically below $0.5 \mu\text{g}/\text{Nm}^3$, requiring injection of elemental Hg to establish a sufficient concentration for meaningful testing. At the same time the nature of the flue gas and ash led to high levels of Hg oxidation in the inlet sampling system and ductwork. As a result, extensive parametric testing with operation over several days at each condition, as has been done to investigate NO_x and SO₂ oxidation and capture, could not be performed. Instead, the investigation was limited to short periods of operation with the reactor alternately energized and de-energized.

Using measurements at the outlet of the system only, oxidation of mercury by the dielectric barrier discharge reactor was tested over a range of energy densities and gas flow rates. The limited testing conducted has shown: (i) increasing energy density in the reactor increases the conversion of elemental mercury, (ii) the oxidation of elemental mercury is not dependant on inlet elemental mercury concentration in the range of 2 – 8 $\mu\text{g}/\text{Nm}^3$, and (iii) increasing the gas flow through the reactor increases the oxidation of elemental mercury.

Testing of the DBD reactor demonstrated that increasing the reactor power density (energy density) from 15 W/scfm to 25 W/scfm increased the elemental mercury conversion from 57% to 75% at a nominal flow rate of 2500 scfm through the reactor. Increasing the energy density in the reactor increases the concentration of oxidizing species produced by the barrier discharge process, increasing the rate of reaction (10). This behavior is consistent with that seen in the conversion of NO to NO₂ and HNO₃, where increasing energy density increases the rate of oxidation.

A test of DBD performance at different inlet mercury levels suggests that the oxidation of elemental mercury is not dependent on the inlet elemental mercury concentration. Elemental mercury concentrations of 2.5 $\mu\text{g}/\text{Nm}^3$ and 6.0 $\mu\text{g}/\text{Nm}^3$ were tested with a flowrate of 1500 scfm and an energy density of 18 watts/scfm resulted in a conversion percentage of 56% \pm 5% and 53 \pm 6%, respectively. This result varies from the behavior exhibited by the reactor for NO_x oxidation. In the case of NO_x, the molar conversion to NO₂ and HNO₃ is constant for a given reactor energy density resulting in a higher conversion percentage as the inlet NO_x concentration is reduced. For example, operation of the discharge reactor to create 100 ppm of HNO₃ from NO will require the same energy input at an inlet NO_x concentration of 200 ppm (resulting in 50% NO_x conversion) as at an inlet concentration of 250 ppm (40% NO_x conversion). For elemental mercury oxidation, in the range that was tested, there was no decrease in conversion percentage with increased elemental mercury concentration. It is thought that at the mercury concentrations present in flue gas, the collision rate between elemental Hg and the oxidizing radicals produced by the reactor is the rate limiting step. Therefore, when the concentration of elemental mercury in the flue gas is increased, the rate of reaction and the conversion efficiency of the reactor also increase.

Parametric testing looking at the effect of velocity through the reactor on the conversion efficiency of elemental mercury showed greater conversion as the gas velocity increased. At an energy density of 15, 20 and 25 W/scfm, increasing the flue gas flow through the reactor from 2000 scfm to 2500 increased the conversion of elemental mercury from 36% to 57%, 46% to 64%, and 42% to 74% respectively. Again, this is in contrast to the mechanism for NO_x oxidation in the DBD reactor. For NO_x, oxidation and conversion efficiency are related to the concentration of NO_x and the energy density of the non-thermal plasma. For mercury, the results show that the increased flow has increased conversion efficiency. This result may be due to increased gas mixing resulting from higher gas velocities.

Testing under this cooperative agreement has shown the ability of the DBD reactor to oxidize elemental mercury in flue gas streams. Unfortunately, the instrumentation did not allow enough measurements to be made and the reactive ash did not allow for enough high elemental mercury conditions to be able to perform parametric testing. Therefore, although the DBD reactor has shown the ability to oxidize elemental mercury, more testing is required to develop the optimized conditions for oxidation of elemental mercury with the DBD reactor at high elemental mercury concentrations.

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6.0 References

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7.0 List of Acronyms

ASN – Ammonium Sulfur Nitrates

CAVkit – Calibration Verification

CEMS – Continuous Emission Monitoring System

DBD – Dielectric Barrier Discharge

ECO – Electrolytic Catalytic Oxidation

ESP – Electrostatic Precipitator

QAQC – Quality Assurance Quality Control

QSI – Quick Silver Inertial Separator

TVM – Total Vapor phase Mercury

WESP – Wet Electrostatic Precipitator

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